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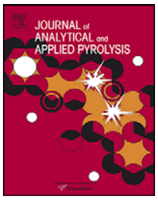

Experimental characterization of gaseous species emitted by the fast pyrolysis of biomass and polyethylene

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ABSTRACT

This study aims to experimentally characterize the carbonaceous and nitrogenous species, from the flash pyrolysis of millet stalks and polyethylene plastic bags, using the device of the tubular kiln, coupled to two gas analyzers: Analyzer Fourier Transform Infrared (FTIR) and an analyzer Infrared Non-Dispersive (IRND). Gaseous products analyzed are: CH_4, C_2H_2, C_2H_4, C_3H_8, C_6H_6, CO, CO_2, NO_2, NO, N_2O, HCN and NH_3. Whatever the temperature of thermal degradation, the pyrolysis shows us that in terms of mass:

- For the millet stalks, the gaseous compounds are formed mainly CO and CO_2 to the carbonaceous species, HCN and NH_3, for the nitrogenous species analyzed;
- As regards the polyethylene bags, hydrocarbons for carbonaceous species and HCN, NH_3 and NO_2 for the nitrogenous species, are most abundant.

In addition, the results suppose that in our experimental conditions, the hydrocarbon which is involved primarily in the formation of CO is ethylene C_2H_4. At the end of this characterization, we determined the rate of carbon and nitrogen found in the volatile gas. With millet stalks we have about 45% of volatile carbon and 15% of the nitrogen of fuel that are found in gaseous products. The results obtained with the plastic bags give 68% carbon and 15% nitrogen found in the nitrogenous species analyzed.

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1. Introduction

Waste management has become a very important environmental issue. Indeed, faced with a continual growth of their mass and volume, and faced their changing composition, the management systems more and more complex are implemented. These lead, for compliance, a higher utilization of waste energy recovery or recycling. Among these processes, incineration of waste is a reliable leading to a reduction in mass and volume of waste and can allow a recovery. Among the different incineration technologies implemented, the kilns grills are still the most widespread, being adapted to a wide variety of waste. However, incineration may be generator of pollution. The exhaust emissions consist of carbon oxides, sulphur, nitrogen, chlorine products (dioxins and furans), volatile organic compounds, polycyclic aromatic hydrocarbons, dust. The gas pollution comes in addition to any generated by all combustion processes, resulting in environmental problems and public health of the highest order. It becomes capital of reducing pollutants and environmental impact of combustion processes, which represents a considerable challenge current. Reducing the impact generated by the gaseous pollutants is one of the concern of international organizations, notably with the global conferences such: and more recently. To avoid the transfer of pollution, the processes involved are subject to compliance with emissions standards more stringent. Among the gaseous species emitted, nitrogen oxides and carbon contribute of main problems of our environment and humans: they are partly responsible for the destruction of the ozone layer, the formation of oxidants mist and acid rain and contribute to global warming. Since a number of years, studies are conducted in the Laboratory of Physical and Chemistry of environment, to improve the techniques for reducing emissions of pollutants. This work has an experimental application to the optimization of combustion in order to reduce toxic emissions, and numerical to identify and understand the reaction

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mechanisms of formation and destruction of nitrogen oxides. The identification of the main ways of degradation of the different solids studied and the composition of pyrolysis gases are essential to carry out investigations to supplement the experimental data on the thermal degradation of cellulosic materials and plastic based polyethylene, also for the better understanding the combustion process and the gaseous products degradation. In addition, tests using the fixed bed reactor as well as dimensional analysis which allow the calculation of oxygen consumption show that the degradation of fuel in the fixed bed reactor is done without oxidation reaction of the solid and is similar to a stage of pyrolysis [1]. This study concerns the flash pyrolysis of millet stalks and plastic bags made of polyethylene with the tubular kiln. The term “flash pyrolysis” is because we pre-heat the kiln to the desired temperature of degradation between 800 and 1000 °C, before introducing the fuel. In addition, this type of pyrolysis is due to the small size of the degraded solid, fast speed of introduction of the fuel in the reactor: thus, the rate of rise in temperature can be estimated to 500 °C s^{-1}. This device is coupled to two analyzers: Analyzer Infrared Non-Dispersive (IRND) and an analyzer Fourier Transform Infrared (FTIR). The fuel is mainly composed of carbon, oxygen, hydrogen and nitrogen. The species analyzed are: CH_4, C_2H_2, C_2H_4, C_3H_8, C_6H_6, CO, CO_2, NO_2, NO, N_2O, HCN and NH_3. The HCN and NH_3, are key intermediaries in the formation of NO of the fuel [2–8], while the NO_2 and N_2O are involved in the reduction of NO [3,6–11]. Similarly, hydrocarbons are the precursors to the formation of CO and CO_2 and intervene in the process of formation and destruction of NO [12–14]. This work will identify, according to the operating parameters, volatile species emitted, to understand how these compounds contribute to the formation of major pollutants namely nitrogen oxides and carbon.

1.1. Properties of fuels

An elementary analysis of millet stalks and polyethylene bags, was performed to accurately characterize our fuel and carry out material balances. To do this, samples of each component were analyzed for the determination of the majority elements, i.e.: C, H, O, N, S, Cl, H_2O and ashes. These tests have been carried out by the analysis of the National Center for Scientific Research (CNRS) with five different samples of each fuel. The values presented in Table 1 correspond to the average of rate from 5 analysis by fuel.

The polyethylene bags are made from PE granules, but during the manufacturing process, some molecules can be added to modify the physical properties of the bags. Thus, we have made in Table 2, a comparison of analysis elementary of the polyethylene bags and the pure polyethylene [15–18]. In view of this review, we find that the polyethylene bags have a chemical composition different from that observed with the pure polyethylene. The differences are mainly at the level of carbon, oxygen, chlorine and ash. These differences are related to the addition of adjuvants.

Similarly, the stalks of millet being biomass predominantly composed of cellulose, it is interesting to characterize this fuel by comparing (in Table 3) its elemental composition to that of fir wood, described by [1,19,20]. It appears that the elemental composition of millet stalks is very close to that of wood.

Table 1
Elementary composition of fuels of the study.

Elements	Millet straws	Polyethylene films
Carbon (C)	44.4%	73.8%
Hydrogen (H)	6%	11.5%
Nitrogen (N)	0.3%	0.2%
Sulphur (S)	0.15%	0.2%
Oxygen (O)	43.8%	4.8%
Chlorine (Cl)	814 ppm	300 ppm
Water (H_2O)	4.4%	2.5%
Ashes	0.8%	6.7%

Table 2
Elementary composition of the polyethylene films and pure polyethylene.

Elements	Polyethylene films	Pure polyethylene
Carbon (C)	73.8%	85.4–86.4%
Hydrogen (H)	11.5%	13.5–14.3%
Nitrogen (N)	0.2%	0%
Sulphur (S)	0.2%	0–0.08%
Oxygen (O)	4.8%	0–0.2%
Chlorine (Cl)	30 ppm	0 ppm
Water (H_2O)	2.5%	–
Ashes	6.7%	0%

Table 3
Elementary chemical composition of the wood and the millet straws.

Elements	Dumont T.	Beaumont O.	Rogaume T.	Millet straws
Carbon (C)	49.5%	50.9%	47.6%	44.4%
Hydrogen (H)	6%	5.76%	6.4%	6%
Nitrogen (N)	0.5%	0.2%	0.2%	0.3%
Sulphur (S)	–	0.04%	0.2%	0.15%
Oxygen (O)	43%	42.1%	45.3%	43.8%
Ashes	1%	1%	–	0.8%

1.2. Description of experimental apparatus

The device used is the tubular reactor instrumented to study the thermal degradation of solid materials in pyrolysis and combustion. This device was used to determine for different temperatures, the composition of the volatile gases generated by fast pyrolysis. Fig. 1 presents a diagram of the tubular reactor used.

The central part of the diagram consists of the tubular kiln and the quartz reactor. The kiln is placed horizontally and measure 88 cm long. It is connected to an automatic temperature control (heat resistance) with 1250 °C like maximum instruction. The quartz reactor with a total length of 120 cm and an inside diameter of 7 cm, is partly placed inside the kiln. A thermocouple of type K is placed at its center in order to know the temperature. A basket sample holder (in quartz) is used for the introduction of the fuel inside the kiln.

The flow of oxidizer (nitrogen, “nitrogen + air” or air, depending on the chosen degradation) is performed by a digital control box (ELECTRONIC CONTROLLER 0154) linked to a mass flowmeter of brand BROOKS, type 5850E that allows a maximum flow gas of 30 Nl mn^{-1} with a precision of 10^{-1} Nl mn^{-1}. A fraction of gas from the degradation is directly collected in a Kevlar bag with a capacity of 37 l. The volume of gas collected is calculated by the flow of gas carried and the time of filling the bag. Before each filling, the bag is cleaned and the vacuum is made by aspiration with a pump. The gas collected is then taken continuously with a pump and sent to the gas analyzer with a flow rate of 2 l mn^{-1}. These gases pass through a filter that removes soot and tars. Then they cross a box, by Pelletier effect, which removes water vapor before analysis.

The gases collected in the bag are spread into series toward two types of analyzers:

- Analyzers Infrared Non-Dispersive (IRND) and paramagnetic, of brand Servomex, to measure the concentrations of CO, CO_2, O_2, SO_2, and NO;
- Spectrometer Fourier Transform Infrared (FTIR) brand Thermo Optek NICOLET, type AVATAR, to determine the concentrations of CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_6H_6 and NH_3, HCN, NO, NO_2, N_2O and SO_2.

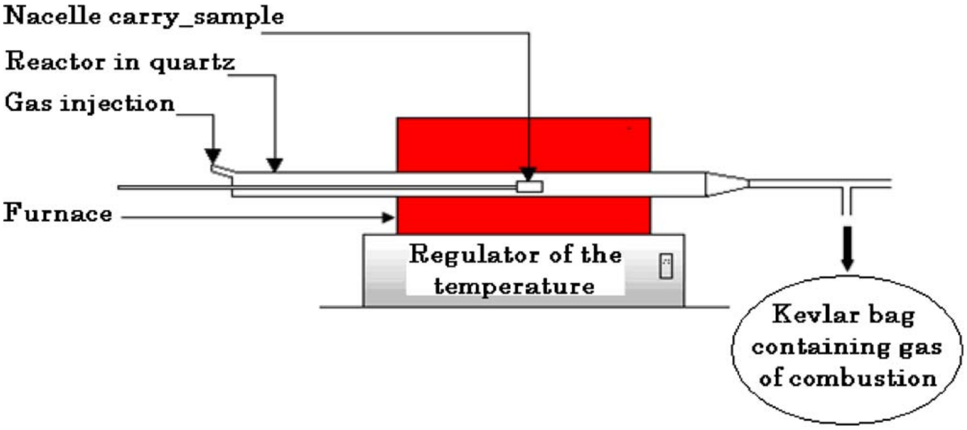

Nacelle carry_sample
Reactor in quartz
Gas injection
Furnace
Regulator of the temperature
Kevlar bag containing gas of combustion

Fig. 1. Device of tubular furnace.

1.2.1. Infrared non-dispersive and paramagnetic analyzers

A suction pump allows the circulation of a flow of smoke of 2 Nl mn^{-1}. The accuracy of the analyzers is of 2% of reading for the analysis of O_2, SO_2 and CO_2, and 5% of the value read for the analysis of CO and NO [21]. The detection limit for NO, CO and SO_2 is 10 ppm and 0.1% for O_2 and CO_2 [22]. The response time of the analyzers is 30 s.

1.2.2. Fourier transform infrared analyzer (FTIR)

Infrared spectrometer used has been established at the Mine school of Albi (France) by Jean-Michel COMMANDRE in its work for doctoral degrees. Since, [23–28] have used this apparatus with this quantification process, for their research works. For qualitative analysis we can say that because of the weak interaction between the molecular gases, the spectrum of a mixture of gases can be considered as a set of pure compound spectra. This allows for two types of product identification in the spectra analysis:

- By visual identification method: this method is to use spectra of pure compounds contained in a commercial library (Aldrich, Sigma);
- Method of personal identification: identification is made by visual layering of strips characteristic of each compound in the spectrum of reference recorded by analysis of standard gases.

We chose to describe the gases of solids pyrolysis by using the method of personal identification.

In the mid-infrared spectrum (wave number between 650 and 4000 cm^{-1}), we selected spectral bands for identification of each of compounds.

The spectrometer was calibrated for the gas we want to quantify: CH_4, C_2H_2, C_2H_4, C_2H_6, C_6H_6, CO, CO_2, NO_2, NO, N_2O, HCN, NH_3 and SO_2. The method used by the software “QUANT PAD” pack OMNIC of Nicolet, allows the simultaneous determination of individual concentrations of many compounds in the mixture. To do this, we must enter the following data:

- The compounds analyzed (gas cited above);
- For each compound, indicate the spectral band in which it will be qualified and quantified;
- The files of standard spectra of all concentrations of each gas.

It is important to note that the method uses to quantify the components, an analysis in the regions (different of the classic methods using the height or peak area). These areas can be subdivided into windows. This method proceeds in two stages: qualitative and quantitative analysis.

For qualitative analysis we compare the spectrum of the sample containing several compounds with spectra of standard gas (usually several concentrations of the same compound).

The quantitative analysis is to calculate the concentration of each compound in the unknown sample by “fittage” of spectrum of pure gas to the spectrum of the sample. The software assigns a multiplier to each spectrum of pure gas present in the unknown mixture. The concentrations of the standard gas are then multiplied by these factors to assess the concentrations of the gas of sample.

Ideally, it is preferable to select the spectral regions for which a single gas absorbs. In fact, by superimposing the spectra of standard gases, it is usually possible to find a spectral zone where only one gas absorbs. However, with regard to hydrocarbons, spectral zones are very close, and it is sometimes difficult to determine a zone where only gas is present.

Table 4 shows the spectral areas where take place the qualification and quantification of each gas. The literature provides spectral areas identical or different, depending on the resolution of the instrument and the nature of the gas mixture analyzed [29–31].

The absorbance does not necessarily vary linearly with gas concentration. Different concentrations of each gas standard must be established to carry out the polynomial of calibration.

To this end, we set up a bench of dilution. This bench of dilution is composed of four thermal mass flowmeters, mounted on a turntable, whose outputs are connected together. The mixer at the outlet of the metering equipment is connected to the heated line, leading the gas to the same temperature as during the experiments of combustion in the cell of gas heated of the FTIR. Thus it was possible to carry out successive dilutions to obtain the different required concentrations of a cylinder of standard gas and add the spectrum of this gas in the database. The standard gases are brand “AGA” and “Air Liquide”, and present a precision between 1 and 5% of the indicated value.

The development of a quantification method starts with the accumulation of sufficient spectra of the same gas at different concentrations (in the operating conditions of pressure and temperature of an identical cell).

Starting from points at different concentrations we can draw the calibration curve. Some gases have little linear responses, and require a large number of calibration points, while for others, two points are sufficient. The calibration curves are represented for each gas, in Figs. 2–12.

We used the bench dilution to achieve:

- 4 concentrations for CH_4.
- 3 concentrations for C_2H_4.

Table 4

Regions of quantification (start and end in cm^{-1}; '–' = Not used to track the gas, I = range where the gas interferes without quantification; S = zone of quantification).

Start	End	CH_4	C_2H_2	C_2H_4	C_3H_8	C_6H_6	CO	CO_2	NO_2	NO	N_2O	HCN	NH_3	SO_2
860	1020	–	–	S	–	–	–	–	–	–	–	–	–	–
990	1015	–	–	–	–	–	–	–	–	–	–	–	S	–
1300	1405	–	–	–	–	–	–	–	–	–	–	–	–	S
1579	1644	–	–	–	–	–	–	–	S	–	–	–	I	–
1851.4	1930.94	–	–	–	–	–	–	–	–	S	–	–	–	–
1969	1978	–	–	–	–	S	–	–	–	–	–	–	–	–
2096.6	2140	–	–	–	–	–	S	–	–	–	–	–	–	–
2140	2223	–	–	–	–	–		–	–	–	S	–	–	–
2860	2920	S	–	–	–	–	–	–	–	–	–	–	–	–
2922	2955	I	–	I	S	–	–	–	–	–	–	–	–	–
3230	3307	–	–	–	–	–	–	–	–	–	–	S	–	–
3285	3320	–	S	–	–	–	–	–	–	–	–	–	–	–
3520	3760	–	–	–	–	–	–	S	–	–	–	–	–	–

- 4 concentrations for C_2H_2.
- 8 concentrations for CO.
- 12 concentrations for CO_2.
- 4 concentrations for NO_2.
- 12 concentrations for NO.
- 4 concentrations for N_2O.
- 2 concentrations for HCN.
- 3 concentrations for NH_3.
- 4 concentrations for SO_2.
- 5 concentrations for C_3H_8.
- 5 concentrations for C_6H_6.

The flow of gas through the cell is 2 Nl mn^{-1}. Measurement accuracy is about 5% of reading for most gases quantified, except for CO_2, for which the accuracy is reliable only for a concentration of less than 1%, i.e. 10^4 ppm. After, quantification is very uncertain and we take the value indicated by the analyzer non-dispersive infrared. The threshold for detection of NO, N_2O and NH_3 is 10 ppm [22]. The response time of the FTIR is 40 s.

2. Method and experimental conditions

The Millet stalks are cut into thin sticks 1.5 cm long and the polyethylene bags into square sheets of 1.5 cm of side with less of 1 mm thick. Samples, with a mass of 500 mg, were then weighed with a precision balance, 10^{-2} mg. These sizes and these masses allow to avoid the effect of temperature gradient at the degradation of the fuel. This physical phenomenon influences the mode of degradation. Indeed, the degradation of a "fuel thermally thick" would imply the presence of a temperature gradient, while that of a "fuel thermally thin" would be no temperature gradient since in this case the temperature is supposed uniform throughout the solid.

The temperature of pre-heating of the kiln is programmed to the desired value. The flow of gas is selected to have a fixed residence times. It is based on the residence time of hot gas and the local temperature of degradation. Once the set temperature is reached and stable, the oxidizing gas flow is set. The flow of oxidizing gas is performed by a digital control box, brand ELECTRONIC CONTROLLER, type 0154, connected to a mass flowmeter brand BROOKS, type 5850E, which allows a maximum flow of gas 30 Nl mn^{-1} with accuracy to 10^{-1} Nl mn^{-1}.

Then, the sample is introduced in the kiln with a basket quartz sample holder. The basket is manually entered into the kiln at a constant speed. It is at the center of the kiln, where the temperature is given by a thermocouple of type K. The gases from the decomposition are transported to the gas analyzer. Before each new test the basket is beforehand removed from the kiln. The response time of the analyzer Fourier Transform Infrared (FTIR) and the analyzers SERVOMEX are high (respectively, 40 and 30 s), the gases from the thermal degradation are stored in a bag of Kevlar of 37 l of capacity. In other words, flow and pressure of gas leaving the reactor are very high for the analyzers which save different concentrations of the gaseous species. The gases collected are then continuously take with a pump (with a rate of 2 Nl mn^{-1}) and sent to the gas analyzers. These gases pass through a filter that removes soot and tars in order to prevent their deposit on cells and/or on other internal components of the analyzers. These deposits can damage the components. The transfer lines of gases, the reactor to the bag and the bag to the analyzers are cleaned (by blowing) after each test, to remove residues of soot and tar. The bag for the collection of the pyrolysis gases is changed every five trials, this will prevent deposits of tar, soot and/or particles that can compromise the reliability of the results by reacting with the gases. The results are treated by computer in real time.

Table 5 shows the various conditions for the tests.

Nitrogen of air (N_2) is carrier gas used because it cannot react with gas devolatilizing for the temperature range of our study. Indeed, the speed of formation of NO is directly related to the energy needed to break the link N–X [32,33]. In addition [34], shows that the formation of thermal NO involves molecular nitrogen from the air. Its production is in the flame and requires the input of a high energy to break the triple bond. This energy can be attained only at temperatures above 1250 °C. Our temperature conditions correspond to those used in the thermal degradation of mixtures of cellulosic and plastic materials [1,35–40]. The residence time of gases in the hot zone of the reactor was chosen so that the airflow is not too important: given the mass of each sample, a flow too high would imply an only partial pyrolysis of fuel. Indeed, an air flow promotes a very significant cooling of the reaction mixture and a residence time of hot gas too short, and this would cause a decrease in temperature of degradation and an incomplete degradation of fuel.

3. Results

The main objective is the identification of the nitrogenous and carbonaceous species generated by pyrolysis of millet stalks and polyethylene bags.

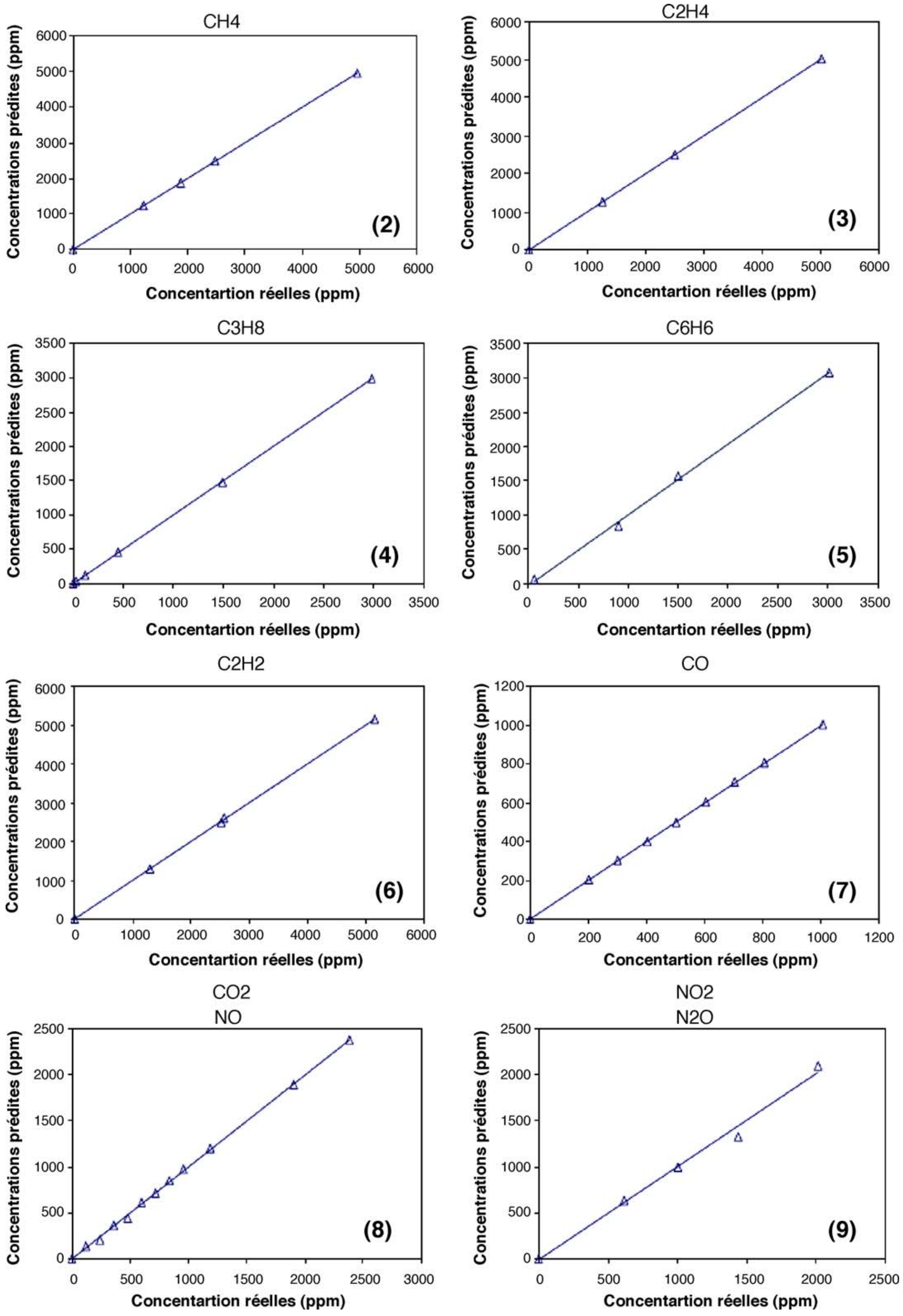
3.1. *Pyrolysis of millet stalks*

3.1.1. *Carbon*

Fig. 13 shows the emissions of the carbon, analyzed during the pyrolysis of millet stalks in our experimental conditions. Table 6 also shows, for each temperature, the percentage of carbon converted into each one of the gaseous compounds analyzed. The results are expressed in milligrams of the species produced per gram of fuel of degradation.

Under inert atmosphere, millet stalks decompose mainly into carbon monoxide (CO) and carbon dioxide (CO_2). We also find that hydrocarbons such as benzene (C_6H_6), ethane (C_2H_6) and propane (C_3H_8) are hardly produced in our experimental conditions.

The more the temperature increases the more the content of CO and CO_2 in smoke rises. We can explain this by the presence of oxygen in fuel (43.8%). Indeed, the more temperatures is high (with a long residence time) the more the C=O bond of fuel is likely to break and release oxygen of the fuel. These conditions favour the hydrocarbons oxidation into CO. Moreover, it is shown that the CO_2 comes mainly from the oxidation of CO [41–46], but with a speed of oxidation lower than that of hydrocarbons into CO, [43–47]. The presence of hydrocarbons will inhibit the oxidation of CO [48], the formation of CO_2 will take place after the oxidation of



Figs. 2 to 12. Calibration curves of the gas to analyze on the FTIR.

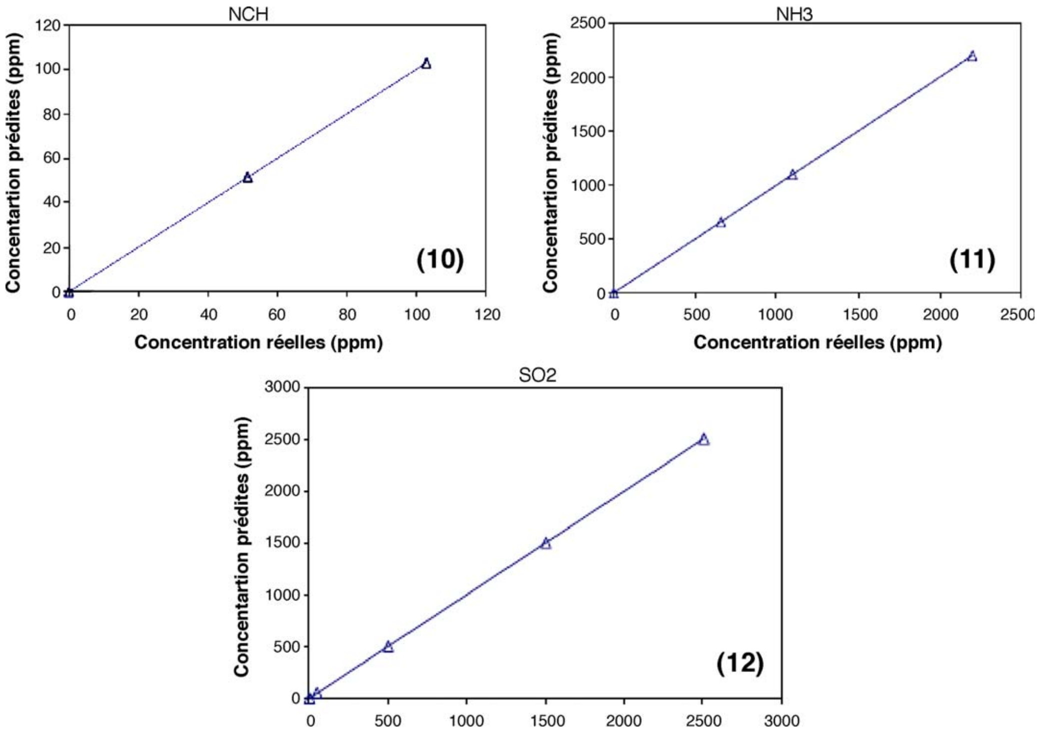


Fig. 2. (*Continued*).

hydrocarbons into CO. However, during our testing, the residence time of gases in reaction zone is quite long (2 s) so the CO formed is partially oxidized to CO_2.

We also observe an increase in the content of methane (CH_4) and acetylene (C_2H_2) according to the temperature, while the content of ethylene (C_2H_4) decrease slightly. This suggests that the formation of carbon monoxide comes in part from the oxidation of ethylene. When we refer to the mechanisms of formation and reduction of CO, we see than those from ethylene and in the presence of O_2, $O^•$ and $OH^•$ are dominant [45].

Chemical analysis allows us to see that the millet stalks (like wood) are degraded to form 80% of volatile matter and 20% of fixed carbon. At the end of each test the carbon residue is weighed and for each test the result represents approximately 20% of the initial mass. The results of elemental analysis lead us to assume that the char is composed mainly of carbon [49].

In our experimental conditions, pyrolysis of the millet stalks shows that on average, 19–26% of the carbon is in the form of CO, 7–12% into CO_2 while 15–18% is in the form of light hydrocarbons, mainly CH_4 (7–9%). These results are in good agreement with the bibliography [50–53] note rates of CO close to 45%, 12% for CH_4, 2% for C_2H_2, 3% for C_2H_4 and 0.1% for C_2H_6, during the fast pyrolysis of biomass between 600 and 1000 °C.

From the results of the literature [54], found that in these experimental conditions, approximately 5% of the carbon in the wood is in the form of CO_2. In our case, we obtain a conversion efficiency slightly higher due to the presence of hydrogen [55] and by the fact that in our study, the residence time is higher and long enough for the carbon monoxide is oxidized to carbon dioxide: the formation of CO comes mainly from the oxidation of hydrocarbons

Table 5
Operating conditions of pyrolysis of the millet straws and plastic films.

Type of degradation	Mass sample (mg)	Temperatures (°C)	Flow of gas (Nl min^{-1})	Residence time (s)
Pyrolysis	500	800	11.2	2
Pyrolysis	500	850	10.7	2
Pyrolysis	500	900	10.2	2
Pyrolysis	500	950	9.8	2
Pyrolysis	500	1000	9.4	2

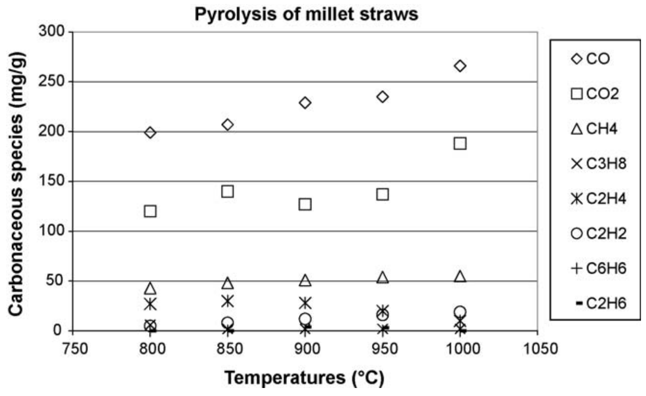


Fig. 13. Rate of the carbonaceous gaseous species emitted during the pyrolysis of the millet straws according to the temperature.

Table 6
Mass percentage of conversion of carbon during the pyrolysis of the millet straws according to the temperature.

	% of volatile carbon in each gaseous compound				
	800 °C	850 °C	900 °C	950 °C	1000 °C
CO	19%	20%	22%	23%	26%
CO_2	7%	9%	8%	9%	12%
CH_4	7%	8%	9%	9%	9%
C_3H_8	1%	0.4%	0.3%	0.4%	0.4%
C_2H_4	5%	6%	6%	4%	2%
C_2H_2	1%	2%	2%	3%	4%
C_6H_6	0%	0%	0%	0%	0%
C_2H_6	0%	0%	0.8%	0.5%	0%
Total	40%	45.4%	48.1%	48.9%	53.4%

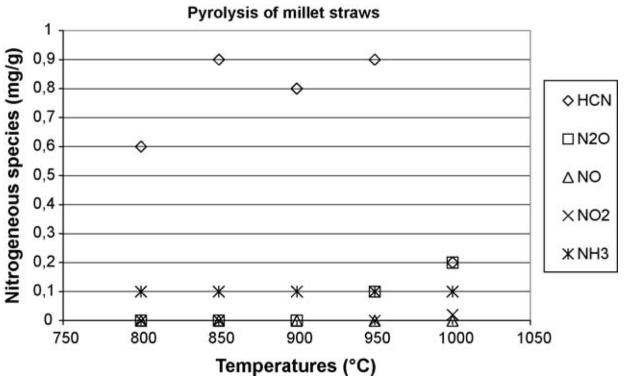


Fig. 14. Rate of the nitrogeneous gaseous species emitted during the pyrolysis of themillet straws according to the temperature.

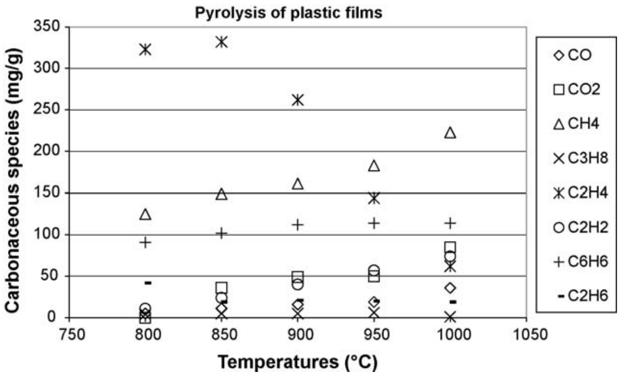


Fig. 15. Rate of the carbonaceous gaseous species emitted during the pyrolysis of the plastic films according to the temperature.

[45,56–60], while the majority of CO_2 comes from the oxidation of CO, as reflected in the studies of [41–46]. However the oxidation of hydrocarbons into CO is faster than those of CO into CO_2. But, a residence time sufficiently long and the presence of hydrogen can increase the yield of oxidation of CO into CO_2. Thus, 41–53% of the carbon released during the pyrolysis of millet stalks is detected in the products tested. We also found during the pyrolysis the production of soot, justifying the fact that a significant part of the carbon is not present in the gases analyzed.

3.1.2. Nitrogen

Fig. 14 shows the emissions of nitrogenous compounds measured during the pyrolysis of millet stalks, for temperatures ranging from 800 to 1000 °C and a residence time of 2 s. We have also presented in Table 7, the conversion rate of nitrogen of the fuel for the conditions tested.

The emissions are low since the content of all the compounds analyzed are lower to 0.9 mg g^{-1}. During this investigation, we did not detect the nitrogen monoxide (NO), while traces of N_2O and NO_2 occur at a temperature of 1000 °C. Hydrogen cyanide (HCN) and ammonia (NH_3) remain the most important compounds in terms of mass and this, whatever the temperature of degradation:

- The average of rate of conversion of nitrogen into HCN is 4–16%.
- About 3% of nitrogen is emitted as NH_3.

When we point of all species measured, 16% of nitrogen content in the millet stalk was found in the compounds analyzed. This low conversion rate is due to the low content of nitrogen in the fuel (0.2%). Moreover, the detection limit of the analyzers is 10 ppm, it is possible that some nitrogen compounds were not taken into account.

3.2. Pyrolysis of polyethylene bags

3.2.1. Carbon

In this section Fig. 15 shows the results of carbonaceous species produced during the pyrolysis of polyethylene bags. Table 8 presents a review on the conversion rate of carbon in each of the volatile compounds analyzed.

Table 7
Rate of nitrogen detected during the pyrolysis of the millet straws.

	% of nitrogen in each gaseous compound				
	800 °C	850 °C	900 °C	950 °C	1000 °C
HCN	10%	16%	13%	15%	4%
N_2O	0%	0%	0%	3%	4%
NO	0%	0%	0%	0%	0%
NO_2	0%	0%	1%	0%	0.2%
NH_3	2%	4%	4%	4%	2%
Total	12%	20%	18%	22%	10.2%

Table 8
Mass percentage of the carbon converted during the pyrolysis of plastic films.

	% of volatile carbon in each gaseous compound				
	800 °C	850 °C	900 °C	950 °C	1000 °C
CO	0.3%	0.7%	0.9%	1%	2%
CO_2	0%	1%	2%	2%	3%
CH_4	13%	15%	16%	19%	23%
C_3H_8	0.5%	0.6%	0.6%	0.7%	0.1%
C_2H_4	38%	39%	30%	17%	7%
C_2H_2	1%	3%	5%	7%	9%
C_6H_6	11%	13%	14%	14%	14%
C_2H_6	5%	2%	2%	2%	2%
Total	68.5%	74.3%	70.5%	62.7%	60.1%

The carbon coming from the pyrolysis of plastic bags is predominantly expressed in the form of light hydrocarbons (C_2H_4 and CH_4) and heavy (C_6H_6). The rates of CO and CO_2 are much lower than those encountered during the thermal degradation of millet stalks, which can be explained by the low presence of oxygen within the fuel. Nevertheless, we have an increase in their rate when the temperature increases. This growth is also observed for CH_4 and C_2H_2. The Decreasing of rate of C_2H_4 lead us to believe that it is the hydrocarbons which mainly participates in the formation of CO. As regards the rate of conversion of carbon, more than 50% of the carbon was converted into light hydrocarbons (C_2H_4 and CH_4) and heavy hydrocarbons (C_6H_6). At the time of their works of simulation [61], have used the experimental results of the University of Zaragoza on the pyrolysis of polyethylene pure, with residence times between 0.81 and 1.45 s and temperatures of 800 and 850 °C. These results are in good agreement with ours, with the predominantly species which are light hydrocarbons such as C_2H_4, CH_4 and C_2H_6 and low production of hydrocarbons of type C_3 and C_4.

On average just over 67% of the carbon released during the pyrolysis of plastic is found in the products tested.

We have noticed during our tests, the formation of tars during the pyrolysis of plastic bags. The bibliography indicates that tars are mostly composed of hydrocarbons heavy [62], which can justify the conversion rate obtained.

3.2.2. Nitrogen

The results (in mg g^{-1}) on emission of nitrogen and the conversion rate of nitrogen in each gaseous compound during the pyrolysis of polyethylene between 800 and 1000 °C with a residence time of 2 s, are, respectively, presented in Fig. 16 and Table 9.

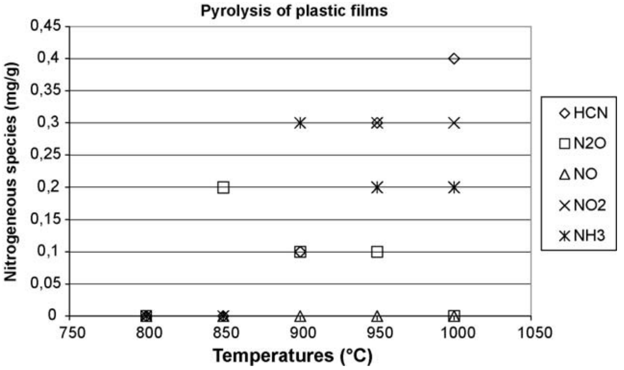


Fig. 16. Rate of the nitrogeneous gaseous species emitted during the pyrolysis of the plastic films according to the temperature.

Table 9
Rate of nitrogen detected in gases during the pyrolysis of the plastic films.

	% of nitrogen in each gaseous compound				
	800 °C	850 °C	900 °C	950 °C	1000 °C
HCN	0%	0%	2%	7%	11%
N_2O	0%	6%	2%	3%	0%
NO	0%	0%	0%	0%	0%
NO_2	0%	0%	5%	4%	4%
NH_3	0%	0%	11%	10%	8%
Total	0%	6%	20%	24%	23%

The average emissions of nitrogen compounds are very low, lower to 1 mg g^{-1} and sometimes even nil. Thus, at 800 °C, no nitrogen compound is detected. Emissions of nitrogen species occur mainly from 900 °C. Similarly to millet stalks, our analyzers cannot detect nitrogen monoxide (NO). This is probably due to the low nitrogen content in the fuel and therefore low emissions, lower to the detection limit of the gas analyzers.

The thermal decomposition of polyethylene produces mainly NH_3 and little of HCN and NO_2. The conversion rates remain low regardless of the compound: 2–11% for all temperatures tested. For all the compounds analyzed, the conversion rates are between 0 and 24% depending on the temperature of pyrolysis. During combustion of the mixtures of cellulosic and plastic materials [15], show that hydrogen cyanide (HCN) leads to the formation of $NCO^\bullet$ and/or $NH^\bullet$ by reactions of first-rate. This leads us to believe that the residence time is sufficiently long for the HCN, in the presence of radicals hydroxy ($OH^\bullet$), can lead to the formation of $NCO^\bullet$ and $NH^\bullet$ [15–17], implying the low conversion rates obtained in our analysis.

4. Conclusion

In this paper, we experimentally characterized the nitrogenous and carbonaceous species coming from the pyrolysis of millet stalks and polyethylene. The experimental device used is the tubular kiln, coupled to analyzer Fourier Transform Infrared (FTIR) and an analyzer Infrared Non-Dispersive (IRND). Gaseous products analyzed during the thermal degradation of millet stalks and plastics bags are light hydrocarbons (CH_4, C_2H_2, C_2H_4 and C_3H_8), benzene (C_6H_6), carbon oxides (CO and CO_2) and some nitrogenous compounds (NO_2, NO, N_2O, HCN and NH_3). Whatever the temperature, the pyrolysis allows us to see, in terms of mass:

- For the millet stalks, the compounds formed mainly are CO and CO_2 for the carbonaceous compounds, and the NH_3 and HCN for the nitrogenous compounds;
- Regarding the polyethylene plastic, hydrocarbons for carbonaceous species and HCN, NH_3 and NO_2 for gases including nitrogen, are most abundant.

Moreover, this work suggests that in our experimental conditions, the hydrocarbon which is involved primarily in the formation of CO is ethylene (C_2H_4). At the end of this characterization, we determined the rate of carbon and nitrogen found in the gases. The tests with millet stalks show us that on average 45% of carbon and 15% of nitrogen are detected in gaseous products. The results obtained with the plastic bags indicate that 68% of carbon and 15% of nitrogen are found in the form of species analyzed.

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